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Research Article

Nanostructured TiO_2 Doped with Nb as a Novel Support for PEMFC

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Nowadays, one of the major issues of the PEMFC concerns the durability. Historically, carbon has been used as a catalyst support in PEMFC; nevertheless, under the environmental conditions of the cell, the carbon is oxidized, leaving the catalyst unsupported. In order to increase the stability and durability of the catalyst in the PEMFC, a novel nanostructured metallic oxide support is proposed. In this work, TiO_2 was doped with Nb to obtain a material that combines chemical stability, high surface area, and an adequate electronic conductivity in order to be a successful catalyst support candidate for long-term PEMFC applications. The TiO_2-Nb nanostructured catalyst support was physically and electrochemically characterized. According to the results, the TiO_2-Nb offers high surface area and good particle dispersion; also, the electrochemical activity and stability of the support were evaluated under high potential conditions, where the TiO_2-Nb proved to be much more stable than carbon.

1. Introduction

In the last decade, several improvements have been achieved regarding the proton exchange membrane fuel cells (PEMFC). Such advances permitted a signific nt increase in the energy conversion efficie y at the same time that the production costs were decreased, placing the PEMFC as one of the best candidates for powering electrical mobile applications [1–4]. In a typical PEMFC, hydrogen fuel is oxidized in the surface of a catalyst and split into protons and electrons; the charge of protons is transported by means of complex phenomena through a polymeric electrolyte [5] while the electrons fl w by an external circuit towards the cathode where they combine together with oxygen to produce water. In the last years, large improvements have been achieved in the development of new materials for PEMFC which allowed an important cost reduction and an increase in the energy conversion efficie y [1]. Nevertheless, problems related to durability, particularly of the catalyst support, are some of the major issues that must be solved to achieve a commercial competitive PEMFC technology [6–9]. In this respect, the department of energy has set a target for the PEMFC, in which these devices should achieve a life time of at least 5000 h in order to be commercially attractive [10]. Consequently, the materials of the PEMFC must be able to operate for long periods of time without degradation, maintaining the performance and more important the output voltage unaff cted.

1.1. Catalyst Supports for PEMFC. Historically, carbon has been used as catalyst support in PEMFC because of their high active area and adequate electronic conductivity [11,

12]; however, it has been proved that under the PEMFC cathode conditions carbon is oxidized, leaving the catalyst unsupported and causing particles agglutination or even its migration out of the electrode [8, 13, 14]. One of the materials that have been proposed as a successful alternative to carbon support is titanium dioxide (TiO_2). TiO_2 is a relatively aff rdable and easy to synthesize material that exhibits high surface area, good affinity with catalytic noble metals, and high electrochemical stability even in PEMFC cathode conditions [9, 15–17]. One of the drawbacks of TiO_2 is its low electronic conductivity [18–20]. To overcome this problem, the TiO_2 has been doped with a number of elements as an approach to increase its electronic conductivity. It has been observed that the insertion of ions in the TiO_2 structure has a double positive effect in the material properties. In one hand, the inclusion of pentavalent ions contributes to diminishing the number of trivalent defects in the material, increasing their chemical stability; also, there is evidence that many of these ions occupy substitutional sites by replacing the Ti atoms in the structure; as a consequence, the material attains an excess of electronic charge carriers and exhibits an n-type semiconductor properties with electronic conductivities several orders of magnitude higher than TiO_2 unmodifie [21–23]. In this work, the TiO_2 was doped with Nb as an approach to obtain a material that combines all the desirable catalyst support properties along with a remarkable electrochemical stability for its utilization in long-term PEMFC applications.

2. Material and Methods

Th Pt/TiO_2-Nb (30 Wt% of Pt) samples were synthesized by the Sol-Gel method using Ti (IV) isopropoxide and Nb (V) ethoxide as precursors. For this procedure, 16.50 mL of Ti (IV) isopropoxide (97%, Sigma-Aldrich) and 1.35 mL of Nb (V) ethoxide (99.95%, Aldrich) were dissolved in 100 mL of 2-propanol at room temperature, in order to obtain a solution with a 10 Wt% of Nb content respecting to the Ti. When the precursors were completely dissolved, 40 mL of deionized water was added to accomplish the following reactions [24]:

Hydrolysis

$$C_{12}H_{28}O_4Ti + 4H_2O \longrightarrow Ti(OH)_4 + 4\left(CH_3CH_2CH_2OH\right) \quad (1)$$

Condensation

$$Ti(OH)_4 \longrightarrow TiO_2 \cdot H_2O + H_2O \quad (2)$$

Hydrolysis

$$2Nb\left(OC_2H_5\right)_5 + 10H_2O \longrightarrow 2Nb(OH)_5 + 5\left(CH_3CH_2CH_2CH_2CH_2OH\right) \quad (3)$$

Condensation

$$2Nb(OH)_5 \longrightarrow Nb_2O_5 \cdot 5H_2O \quad (4)$$

Afte the reaction, a white gel is obtained and let under stirring for 12 h, then filtered and dried at 120°C in vacuum for 10 h. The resulting white powder was thermally treated for 2 h in air at 400°C with a heating rate of 5°C/min.

Th Pt nanoparticles were synthesized and directly supported on the TiO_2-Nb by the chemical reduction method [26]. To obtain 2.00 g of catalyst powder with 30 Wt% of Pt, 1.50 g of $H_2PtCl_6 \cdot 4H_2O$ (99.999%, Alfa-Aesar) was dissolved in 100 mL of deionized water at 50°C; then 2.00 g of TiO_2-Nb with a 10 Wt% of Nb content was added and stirred for 40 minutes; after that, the Pt ions were reduced by adding drop by drop 20 mL of $NaBH_4$ 0.2 M; then the solution was stirred at 50°C during 2 h. Th supported catalyst was filtered and rinsed with deionized water and treated at 400°C under 100% H_2 atmosphere in order to obtain the desired structure and to remove any trace of by-products from the surface of the catalyst.

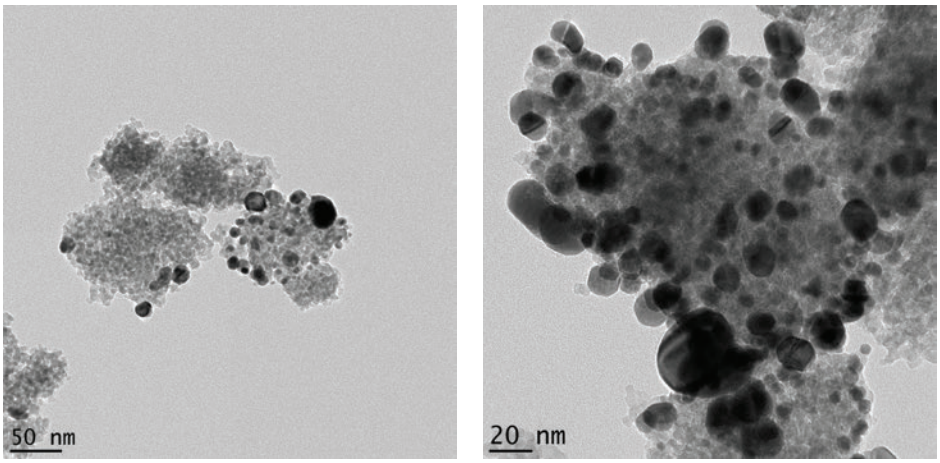
Then in order to determine the composition and structure, the Pt/TiO_2-Nb was analyzed by XRD and TEM, the surface area of the material was determined by nitrogen absorption, and the electrochemical activity was studied by cyclic voltammetry and compared with the performance of a Pt/C sample.

2.1. Physical and Electrochemical Characterization. Th Pt/TiO_2-Nb powders were analyzed in a Jeol 205 Transmission Microscope in order to determine its dispersion, particle size, and morphology. Also a Pt/C sample prepared under the same conditions was analyzed as reference. Th crystallite size and composition of the Pt/TiO_2-Nb and Pt/C samples were determined by X-ray diffraction (XRD) in a Philips Analytical X-Ray X'Pert MPD equipment (50 kV and 40 mA) using a Cu Kα radiation's wavelength of 0.1542 nm. After physical characterization, the electrochemical activity and stability of the catalyst were determined by cyclic voltammetry under the conditions described below.

Th electrochemical characterization was performed in H_2SO_4 0.5 M at 25°C in a 3 electrodes electrochemical cell with an EG&G Princeton 273 Potentiostat. Prior to any measurement, the electrolyte was deaerated by bubbling N_2 for 2 h. A catalytic ink was prepared by mixing 20 μg of Pt/TiO_2-Nb and 25 μL of liquid Nafion in 0.5 mL of 2-propanol; after that, the mixture was ultrasonically stirred by 20 minutes and the working electrode was prepared by placing 20 μL of this ink over a glassy carbon electrode and dried at 50°C for 20 minutes. A Pt grid was used as counter electrode and the potential was measured against a saturated Hg/Hg_2Cl_2 electrode; nevertheless, all the plots show the potential referred to the standard hydrogen electrode (SHE). All the measurements of cyclic voltammetry were recorded at 10 mV/s for 10 cycles and only the last cycle is presented.

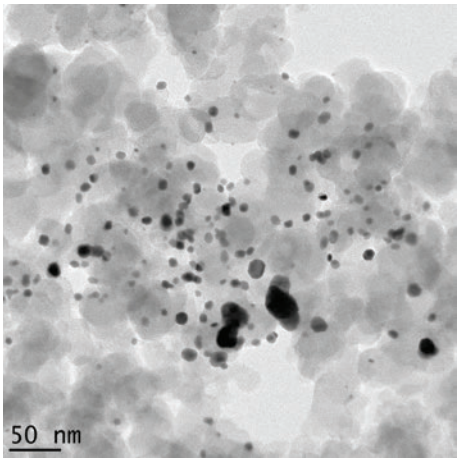
3. Results and Discussion

3.1. Microscopy and XRD. Th TEM micrographs for the Pt/TiO_2-Nb are shown in Figure 1, while the results for the Pt/C sample are presented in Figure 2 as reference. The surface area for the Pt/TiO_2-Nb obtained by nitrogen absorption was 155 m^2/g. This high surface area was correlated with



(a) (b)

Figur e 1: Th TEM micrographs of Pt/TiO_2-Nb at low and high magnific tion. Th nanometric characteristic of support can be observed along with a good distribution of Pt particles on its surface.



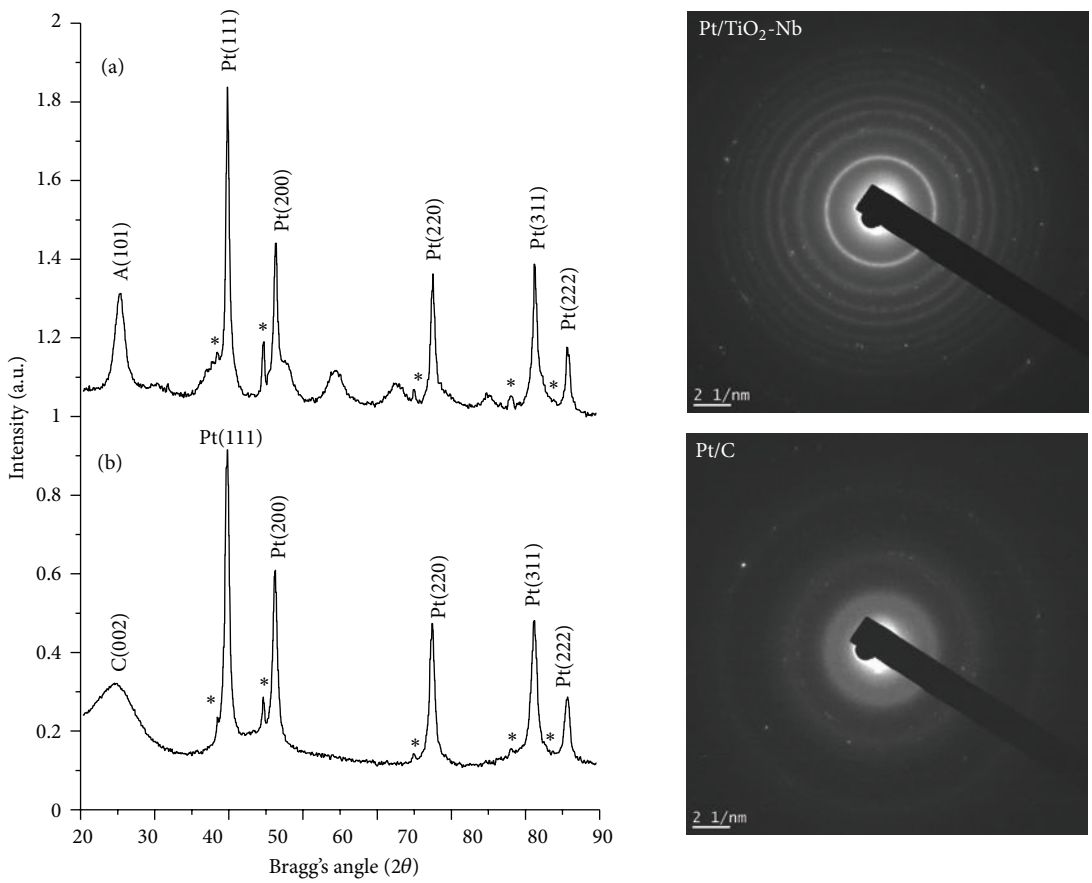
Figur e 2: TEM micrograph of Pt/C as reference. Pt/TiO_2-Nb and Pt/C exhibit similar characteristics, with spherical Pt particles well dispersed over the support and a particle mean size of 15 nm.

the TEM observations that show a nanometric support with well-dispersed Pt particles on their surface. Th mean Pt particle size was calculated and estimated in 15 nm (±4 nm) both for Pt/TiO_2-Nb and for Pt/C.

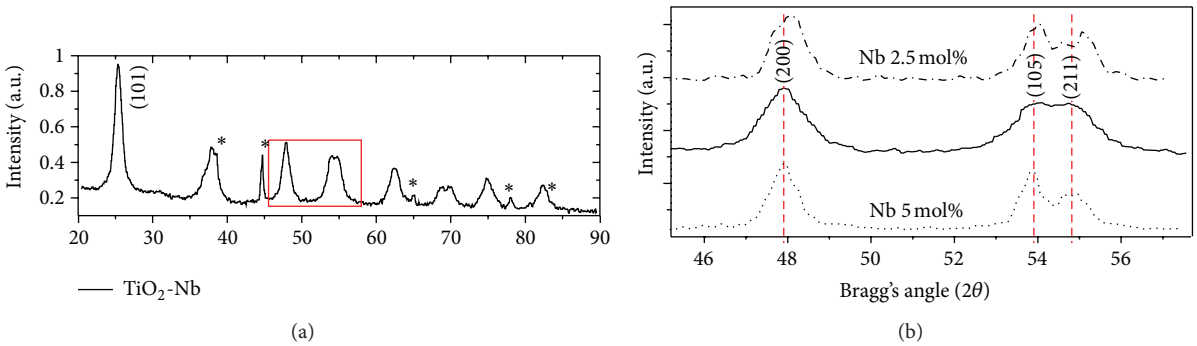
Th XRD patterns of Pt/TiO_2-Nb and Pt/C (Figure 3) revealed peaks that clearly match with the (111),(200), (220), (311), and (222) planes indexed for Pt in its face centered cubic structure (JCPDS 04-0802). With respect to the catalyst supports, the Pt/TiO_2-Nb diffractogram solely permits to identify unequivocally the (101) plane of body centered tetragonal TiO_2 in the form of anatase (JCPDS 21-1272). An additional XRD pattern of the TiO_2-Nb support exposed also the (200), (105) and (211) planes for anatase, as illustrated in Figure 4. In both Pt/TiO_2-Nb and TiO_2-Nb diffractograms, all of the crystallographic planes of Nb (JCPDS 35-0789) are intrinsically convoluted with those of anatase, which precludes their lone observation. However, Figure 4 allows estimating qualitatively the fraction of Nb that has effectively replaced Ti within the nanocrystalline structure. According to the comparison made with previous work on Nb-doped TiO_2, [25] the Nb mole fraction is in a range between 0.025 and 0.050. As a matter of fact, the XRD pattern is closely similar to that exhibited by TiO_2 doped with Nb 5.0 mol%. Indeed, the TiO_2-Nb synthesized support is expected to achieve ca. 6.4 mol%, after an ideally complete replacement of Ti by Nb. Finally, in the case of the carbonaceous support in Pt/C, a broad band ca. 25°, attributed to the (002) plane of turbostratic carbon, is clearly evident in its XRD pattern. Further insight on the crystallographic nature of the Pt-supported catalysts is gained from their transmission electron diffraction patterns, which are shown also in Figure 3. In the case of the Pt/C the diffuse ring diffraction patterns reveal the presence of a material of amorphous nature, such as carbon; although very weak, the three rings correspond to Pt refle tions. The Pt/TiO_2-Nb pattern, on the other hand, exhibits several well-defin d rings characteristics of a polycrystalline material; indeed the brightest diffraction ring denotes that (111)is the preferential orientation of Pt. It is worthy to mention that no evidence of $NbTi_2O_7$ was found according to the employed diffraction patterns database.

Although most of the XRD features observed within the diffractograms result from the sum of two or more single diffraction peaks, it was possible to isolate individual refl ctions for Pt (220) and anatase (101). Therefore, these reflections were chosen to estimate the mean crystallite size according to the Debye-Scherrer equation. Peak fitting analysis on the Pt (220) indicated a crystallite size for Pt of 12.9nm in Pt/C and 13.2 nm in Pt/TiO_2-Nb, both values in agreement with TEM results.

3.2. Electrochemical Evaluation. Th Pt/TiO_2 and Pt/C electrodes were evaluated in H_2SO_4 0.5 M from −0.4 to 1.2 V versus SHE. The results are shown in Figures 5 and 6.



Figur e 3: X-ray diffractograms of the Pt-supported catalysts together with their respective transmission electron diffraction patterns: (a) Pt/TiO_2-Nb; (b) Pt/C. Note: refle tions contributed by the sample holder, made of aluminum, are denoted in all XRD patterns with a star above its corresponding peaks (JCPDS 04-0787).



Figur e 4: (a) X-ray diffractogram of the TiO_2-Nb synthesized support. (b) Zoom in on the detailed XRD pattern, between 45° and 58° 2θ values, which is shown together with two XRD patterns taken and adapted from Lü et al. [25].

In Figure 5 it is possible to observe from the hydrogen absorption/desorption peaks between −0.4 and −0.1 V an evident higher activity for the Pt/C electrode; nevertheless, when reaching the oxidation potentials, the Pt/TiO_2 exhibits a very low anodic current (31.5μA for TiO_2-Nb and 1.37 mA for carbon). Considering that the low anodic current observed for Pt/TiO_2 is a combined result of the low catalyst reactivity for the oxidation of species and the high electrochemical stability of the electrode, it is possible to say that minimum support degradation was observed in Pt/TiO_2 compared with Pt/C electrodes.

Furthermore, when analyzing the irreversibility of the oxidation and reduction peaks for Pt/C (1.2 and 0.4 V), it is possible to see that from the oxidized species at 1.2 V, only the

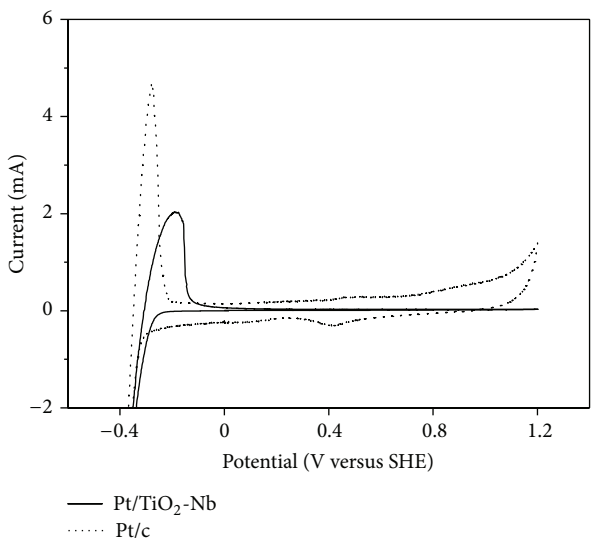


Figure 5: Cyclic voltammograms comparing the electrochemical activity of Pt/TiO_2-Nb and Pt/C in H_2SO_4 0.5 M.

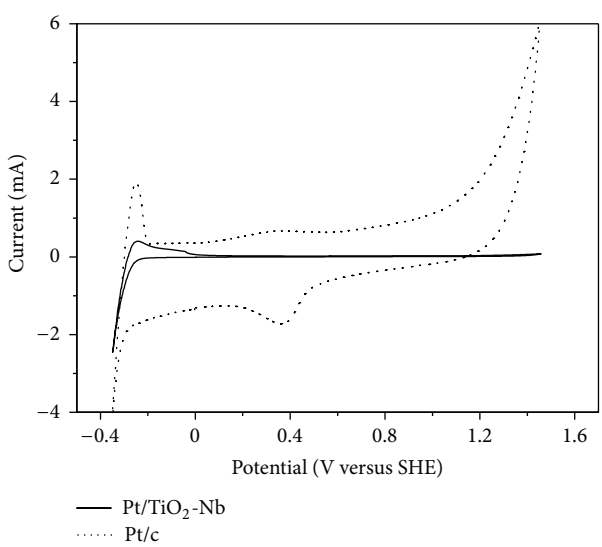


Figure 6: Even at extreme oxidative potentials the electrochemical performance of Pt/TiO_2-Nb remains unaff cted.

fraction that, corresponds to the Pt oxide is reduced at 0.4 V, while a portion of the C support is gasifi d according to the following equation [27]:

$$C + 2H_2O \longrightarrow CO_2 + 4H^+ + 4e^- \quad (5)$$

Th same experiment was repeated and the oxidation potential was increased up to +1500 mV versus SHE (Figure 6). Th response is very similar; again the catalytic activity of Pt/TiO_2-Nb remains lower than Pt/C but, in this case, the accelerated degradation of carbon is much more evident.

4. Conclusions

Th TiO_2-Nb PEMFC electrocatalytic support was prepared and evaluated. The physical characterizations showed a high active area related to its nanostructured composition. When Pt is deposited, the catalytic nanoparticles exhibit good dispersion and homogeneous size and shape, which are desirable characteristics for PEMFC applications. The XRD results show a predominant anatase phase for the TiO_2-Nb and a high crystallite catalyst structure. The voltammograms confi m the TiO_2-Nb outstanding electrochemical stability, even at extreme oxidation conditions; nevertheless, improvements should be made in the support-catalyst electronic contact in order to increase the electrode performance. In the end, the combination of high active area, good Pt affinity, and high electrochemical stability makes the TiO_2-Nb a suitable candidate for further research in order to be utilized as catalyst support in PEMFC.

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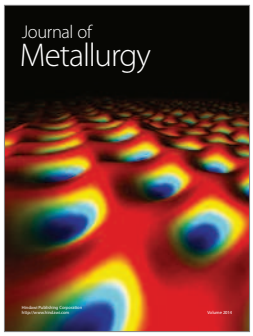

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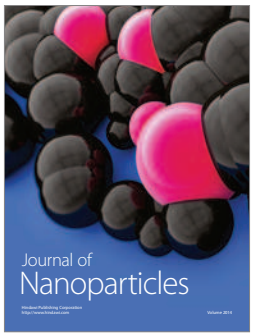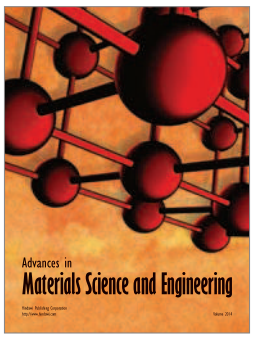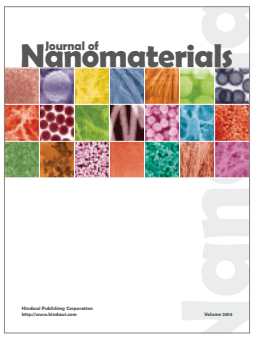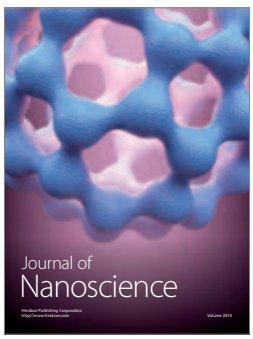
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